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13. ABSTRACT *(Maximum 200 words)*

This project dealt with the study of the reactions of chemical warfare agent simulants with nanoparticulate metal oxides, both as dry powders and as slurries or emulsions with appropriate solvents. Products of these detoxification processes were determined, and the chemical details of how the reactions occurred on the surfaces of the nanoparticles were elucidated. Improved nanoparticle formulations were also developed, that were less sensitive to atmospheric moisture. Biocidal properties of certain nanoparticle materials were also determined.

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Final Progress Report
DAAD 19-00-1-0055
Kenneth J. Klabunde

1. List of Manuscripts

- Wagner, G.W.; Procell, L.R.; O'Connor, R.J.; Munavalli, S.; Carnes, C.L.; Kapoor, P.N.; Klabunde, K.J.; "Reactions of VX, GB, GD, and HD with Nanosize Al_2O_3. Formation of Aluminophosphonates," J. Am Chem. Soc., 123, 1636-1644 (2001).

- Koper, O.; Klabunde, J.; Marchin, G.; Klabunde, K.J.; Stoimenov, P.; Bohra, L.; "Nanoscale Powders and Formulations with Biocidal Activity Toward Spores and Vegetative Cells of *Bacillus* Species, Viruses, and Toxins," Current Microbiology, 44, 49-55 (2002).

- Rajagopalan, S.; Koper, O.; Decker, S.; Klabunde, K.J.; "Nanocrystalline Metal Oxides as Destructive Adsorbents for Organophosphorus Compounds at Ambient Temperatures," Chemistry, A European J., 8, 2602-2607 (2002).

- Jeevanandam, P.; Klabunde, K.J.; "A Study on Adsorption of Surfactant Molecules on Magnesium Oxide Nanocrystals Prepared by an Aerogel Route." Langmuir, 18, 5309-5313 (2002).

- Narske, R.M.; Klabunde, K.J.; Fultz, S.; "Solvent Effects on the Heterogeneous Adsorption and Reactions of (2-Chloroethyl) ethyl Sulfide on Nanocrystalline Magnesium Oxide," Langmuir, 18, 4819-4825 (2002).

- Bedilo, A.F.; Sigel, M.J.; Koper, O.B. Melgunov, M.; Klabunde, K.J.; "Synthesis of Carbon-Coated MgO Nanoparticles," J. Materials Research, 12, 3599-3604 (2002).

2. Scientific Personnel

Alexander Bedilo (postdoc)
Richard Narske (visiting professor)
Shawn Fultz (undergraduate research assistant)
Eric Lucas (graduate student, Ph.D. 2000)
P. Jeevanandam (postdoc, partial support)
K. J. Klabunde (partial summer support)
P. Stoimenov (graduate student, partial support)
P. N. Kapoor (visiting professor)

3. Report of Inventions

A patent disclosure on carbon coated MgO nanoparticles has been submitted.

4. Scientific Progress & Accomplishments

Specific Aims: The goals of this project were to study the destructive adsorption of chemical warfare surrogates and real warfare agents on nanoparticle metal oxides, in order to gain a better understanding of the processes involved (mechanisms), and to determine the products formed. The development of better nanomaterials for these destructive adsorption processes was also an important aspect of the project.

Below, in bullet point form, are shown some of the accomplishments, which have been reported in published and submitted manuscripts.

- Completion of work on the reaction of solid nanoparticle MgO (AP-MgO slurried in pentane with the mimic, paraoxon). By use of solid state NMR it was found that rapid $P-OC_6H_4NO_2$ cleavage occurred. After pentane removal, reaction continued in the solid phase and over about one day both P-OEt bonds were also broken to yield a PO_4 type moiety as residue.
  (Rajagopalan, S.; Koper, O.; Decker, S.; Klabunde, K.J.; <u>Chemistry, A European J.</u>; **8**, 2602-2607, 2002.)

- A series of sorbents were compared and a reactivity (capacity) order with $(EtO)_2P(O)CH_2SC_6H_5$ (DEMTMP) was AP-MgO > CP-MgO > AM (ambersorb) > AC-NO (norite) > AC-CO (activated carbon-coconut shell) > AC-DA (activated carbon-Darco) > CM-MgO (commercial MgO).

- A series of mimics were studied with AP-MgO, including paraoxon, DFP, and DEPTMP. Over time, all P-F and P-O bonds were cleaved on the surface of the MgO, but not P-C bonds.

- Two methods for preparing partially carbon coated nanocrystalline MgO (and other oxides) were devised. The carbon coating tended to give the MgO better ability to operate in moist atmospheres without loss of activity.
  (Bedilo, A.F.; Sigel, M.J.; Koper, O.B.; Melgunov, M.S.; Klabunde, K.J.; <u>J. Materials Chemistry</u>, **12**, 3599-3604, 2002. Also, a patent application is pending.)

- A detailed study of solvent effects on the reaction of 2-CEES with AP-MgO was completed. The least polar solvent pentane was best, and THF and CH_3OH gave slow reactions. In the case of CH_3OH, (methoxyethyl)ethyl sulfide was formed.

- Small amounts of water aided the reaction of 2-CEES with AP-MgO in pentane. Conclusions were that surface –OH groups caused dehydrohalogenation to yield $CH_3CH_2SCH = CH_2$, and substitution of Cl by surface O^{2-} only occurred when surface O^{2-} and surface –OH groups could work together simultaneously.
  (Narske, R.M.; Klabunde, K.J.; Fultz, S.; <u>Langmuir</u>, **18**, 4819-4825, 2002.)

- The first study of the biocidal properties of the AP-MgO·Cl$_2$ adduct (AP-MgO adsorbs chlorine gas to yield a light yellow, active powder) toward anthrax mimics were reported. (Koper, O.B.; Klabunde, J.S.; Marchin, G.L.; Klabunde, K.J.; Stoimenov, P.; Bohra, L.; Current Microbiology, 44, 49-55, 2002.)

- Surfactants interacting with nanocrystalline MgO were studied, with the aim of breaking up aggregates of the MgO and bringing them into solution as colloids. The idea was to "solubilize" the MgO, but while retaining its surface reactivity. Some success was achieved, and the cation surfactant AOT behaved best.
(Jeevanandam, P.; Langmuir, 2002, submitted.) Work in progress on this topic, by Jeevanandam, P. is shown in an attached report.

- A vaporization method has been developed so that nanoparticles of many ionic solids (not just metal oxides) can be prepared on reasonable large scale, such as LiF, MgCl$_2$, MgF$_2$, NaF, etc.

Report of work done by Jeevanandam Pethaiyan:

INTRODUCTION:

The present project involves the study of the effects of adsorbed surfactant on the redispersion behavior and the reactivity of nanocrystalline magnesium oxide. Aerosil OT (AOT) and didodecyl dimethyl ammonium bromide (DDAB) were chosen as examples of anionic surfactant and cationic surfactant, respectively. The redispersion studies were mainly carried out in non-aqueous solvents. The effect of surfactant adsorption on AP-MgO in breaking up the nanocrystalline aggregates was studied by dynamic light scattering (DLS) and visible spectroscopy. The reactivity of surfactant coated AP-MgO compared to bare AP-MgO was illustrated by the destructive adsorption reactions of paraoxon (diethyl 4-nitrophenyl phosphate) and 2-CEES ((2-chloroethyl) ethyl sulfide). These test reactions are widely used to study the reactivity of metal oxide nanoparticles.

AP-MgO nanocrystals isolated in powder form exist as porous aggregates of 1-2 microns in size. The challenge is to break these aggregates down to smaller moieties without substantially hindering the useful reactive surface properties towards acid gases, toxins, etc. Also, in order to explore the chemistry of AP-MgO nanoparticles in colloidal solution, it is necessary to find a way to bring the MgO particle up into a liquid medium and with reasonable colloidal stability. Thus, increasing the stability, dispersability and breaking up of the aggregates of nanocrystalline AP-MgO while maintaining surface reactivity properties is the main purpose of this work.

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EXPERIMENTAL:

AP-MgO was prepared by the aerogel procedure. For the preparation of surfactant adsorbed AP-MgO nanoparticles, typically, about 0.25 g of AP-MgO powder (specific surface area = $450m^2/g$) was suspended in 20 ml of surfactant solutions of known concentrations, prepared using respective solvents (pentane for AOT and toluene, for DDAB adsorption) for about 20 h. The concentration of surfactant solutions and the solvents were chosen from our earlier work on surfactant adsorption on AP-MgO, so that a maximum amount of surfactant would be adsorbed (P. Jeevanandam and K. J. Klabunde, *Langmuir*, 18, 5309, 2002). AP-MgO adsorbs more AOT compared to DDAB under these conditions. After the adsorption, the AP-MgO samples were repeatedly washed with the respective solvent (pentane or toluene) in order to remove the excess surfactants, and dried in a drying cabinet at $100^{o}C$ for about an hour. The surfactant coated AP-MgO samples will hereafter be referred as AP-MgO-AOT and AP-MgO-DDAB. For the redispersion studies, about 100mg of the surfactant coated AP-MgO sample was suspended in 15ml of the solvent of interest and sonicated in an ultrasonic bath for 15 mins. The size of the aggregates in the dispersions was determined by two techniques, namely, dynamic light scattering (DLS) and visible spectroscopy.

Dynamic light scattering (DLS) involves measuring the autocorrelation function, $C(t)$, of the intensity of the scattered light. Fitting the correlation function with exponential yields a correlation time, which is related to the size (radius) of the aggregate by Stokes-Einstein relation. Visible spectroscopy offers an attractive alternative for the characterization of particle suspensions because of its simplicity. In the wavelength range

450nm to 750nm, the decrease in the light intensity of a suspension is usually affected by the scattering of particles provided the particles do not absorb in this region. The empirical expression, $A = K \lambda^{-n}$, holds in this regime. A is the absorbance, K, a factor that includes particle volume and refractive index of the particle and solution, and n is an exponent. If the particle size is smaller than $\lambda/10$ (Raleigh scattering region), then $n = 4$. As the particle size increases, the value of n decreases and in a qualitative sense, 'n' is thus dependent on the average particle size and can be used to trace the aggregation of particles. The value of 'n' can be obtained simply by measuring the absorbance (A) as a function of wavelength (λ) and by plotting log A versus log λ.

To determine how much weight percentage of nanoparticles remains dispersed in the solvent after redispersion (redispersion weight percentage), a gravimetric method was adopted. Typically, about 100mg of surfactant coated AP-MgO nanoparticles was suspended in about 15ml of the solvent of interest, sonicated for 15 mins, and allowed to settle by gravitational sedimentation for various known time intervals. After the elapsed time interval, the supernatant liquid above the sedimentation boundary between the liquid and the solid was syringed out. The remaining solid residue was dried at 100°C and weighed to constant weight. From the difference in the weights before and after the sedimentation experiment, the redispersion weight percentage was calculated.

For the paraoxon adsorption studies, about 100 mg of the surfactant adsorbed AP-MgO sample was placed in a 250 ml round-bottom flask equipped with a magnetic stirrer. Pentane (100ml) and paraoxon (4μl) were added subsequently. The reaction was

monitored by UV-Vis spectrometry by the disappearance of a band at 270nm. The data were collected after 2,5,15 and 20 minutes, and then every 20 minutes upto 3 h. Additional experiments with larger and larger amounts of paraoxon were carried out to find out the capacity of the adsorbent. For the 2-CEES adsorption studies, to 150 mg of the surfactant adsorbed MgO sample, degassed at 150°C under vacuum for 30 min, 10ml of pentane was added. To this about 15μl (0.129mmol) of 2-CEES and about 15μl decane (internal standard) were added. The progress of the destructive adsorption of 2-CEES was followed using gas chromatography.

RESULTS:

It is important to know whether the adsorbed surfactant would still be on the surface of AP-MgO after the redispersion of the surfactant coated nanoparticles in various solvents. The IR spectra of AP-MgO-AOT sample suspended in various solvents for about 3 h, washed and dried, showed that the IR vibrational bands due to AOT molecules are still intact. This indicates that the AOT molecules do not desorb into the solvents in which the surfactant-coated nanoparticles have been redispersed. The size of the aggregates in solution after redispersing the surfactant coated AP-MgO powder in various solvents as measured by DLS is given in Table 1.

Table 1: Size of the aggregates in solution from light scattering (DLS)

Sample	Solvent used for redispersion	Size (r) (nm)
Pure AP-MgO	Ethanol	397
AP-MgO-AOT	Ethanol	464
AP-MgO-DDAB	Ethanol	324

Pure AP-MgO	Water	1979
AP-MgO-AOT	Water	1879
AP-MgO-DDAB	Water	184
Pure AP-MgO	THF	567
AP-MgO-AOT	THF	144
AP-MgO-DDAB	THF	108

It can be noticed that the surfactant coating reduces the size of the aggregates in some solvents. The presence of surfactant molecules on AP-MgO surface prevents agglomeration among AP-MgO nanoparticles and leads to the formation of small clusters of nanoparticles. For example, in tetrahydrofuran, the smallest radii of aggregates were observed (144 nm for AP-MgO-AOT and 108 nm for AP-MgO-DDAB). In water, however, the largest aggregate size was observed for AOT coated AP-MgO nanoparticles. This is probably because, AP-MgO nanoparticles slowly convert to AP-$Mg(OH)_2$ and also the surfactant molecules partition at the aqueous interface. In contrast, the AP-MgO-DDAB sample yields a much smaller aggregate size (184nm) in water. The aggregation behavior of the redispersed surfactant coated AP-MgO nanoparticles in different solvents has also been investigated by transmission spectroscopy. The wavelength exponent "n" for the surfactant coated AP-MgO nanoparticles as measured from the plot of log A versus log λ, for a typical dispersion, is given in Figure 1.
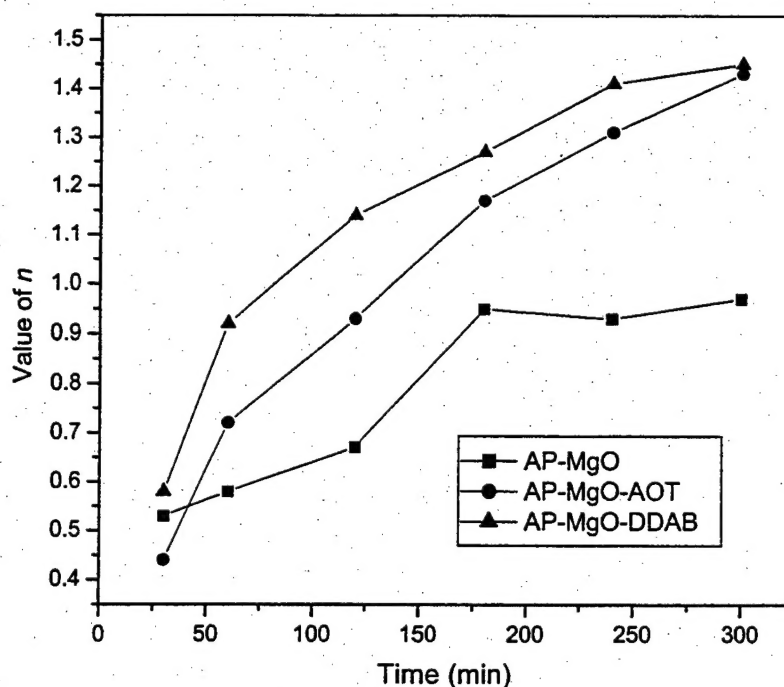
Figure 1: Variation of '*n*', which is the indicator of the size of the aggregates in solution

as measured from a log A versus log λ plot, with time in THF.

It can be seen that the highest *n* values (i.e. the smallest aggregates) are observed for the

surfactant coated AP-MgO nanoparticles. This observation corroborates with the results

obtained by DLS.

The initial screening suggested that a few solvents are better for maximum amount of

redispersion. These solvents were 1-propanol, 1-butanol, THF and methanol.

Determination of redispersion weight percentage as a function of time was further carried

out for these solvents and a typical result is given in Figure 2.
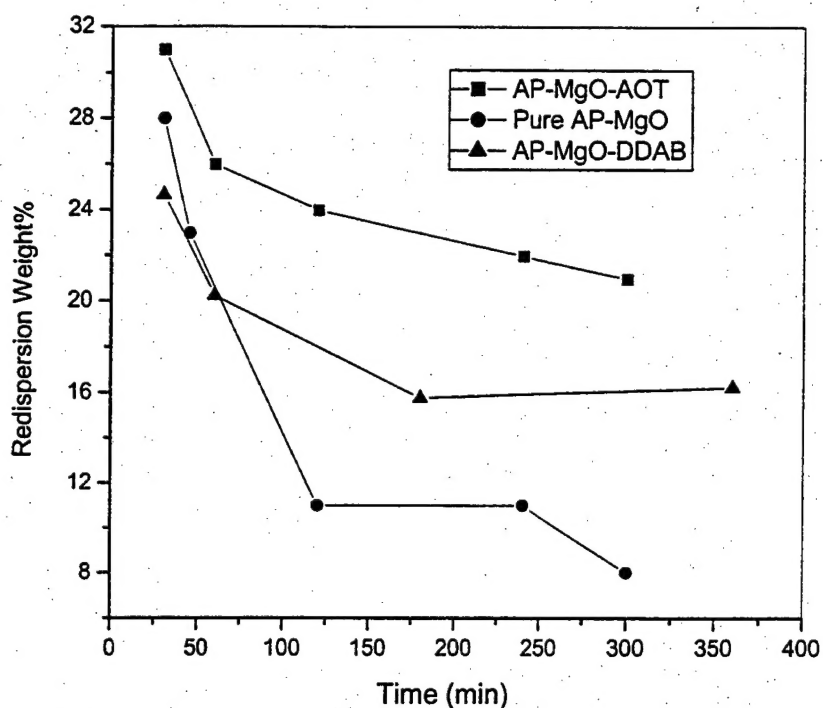
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Figure 2: Redispersion weight percentage as a function of time for surfactant adsorbed AP-MgO samples redispersed in 1-Propanol.

In all the solvents, the surfactant coated AP-MgO nanoparticles were found to disperse better compared to bare AP-MgO nanocrystals. In addition, the AP-MgO-AOT sample showed a higher redispersion weight percentage compared to AP-MgO-DDAB in most solvents studied except in the case of THF where the opposite was found to be true. The facts that 1-propanol and 1-butanol were the best solvents suggest that lengthy alkyl groups of the solvents are necessary for solubilization. It was found that 1-propanol and 1-butanol are the best solvents for redispersion upto 9 h.

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The surfactant adsorbed AP-MgO nanoparticles adsorb paraoxon destructively and the samples were yellow in color owing to the presence of p-nitrophenolate ion on the surface. The results of paraoxon adsorption are shown in Figs. 3 (AP-MgO-AOT) and 4 (AP-MgO-DDAB) and in Table 2. It can be seen that the absorbance due to paraoxon (270 nm) decreases as a function of time. It was found that about 12 μl of paraoxon is adsorbed by about 100mg of AP-MgO-AOT and about 7 μl of paraoxon is adsorbed by 100 mg of AP-MgO-DDAB sample (pure AP-MgO adsorbs about 16 μl paraoxon/ 100mg AP-MgO). The reactivity trend for the destructive adsorption of paraoxon was AP-MgO > AP-MgO-AOT > AP-MgO-DDAB.
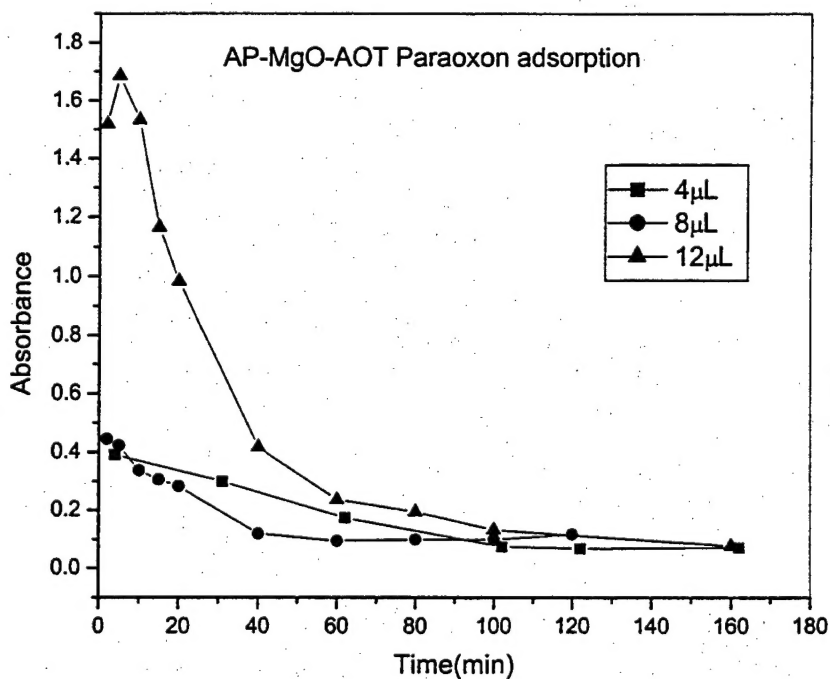

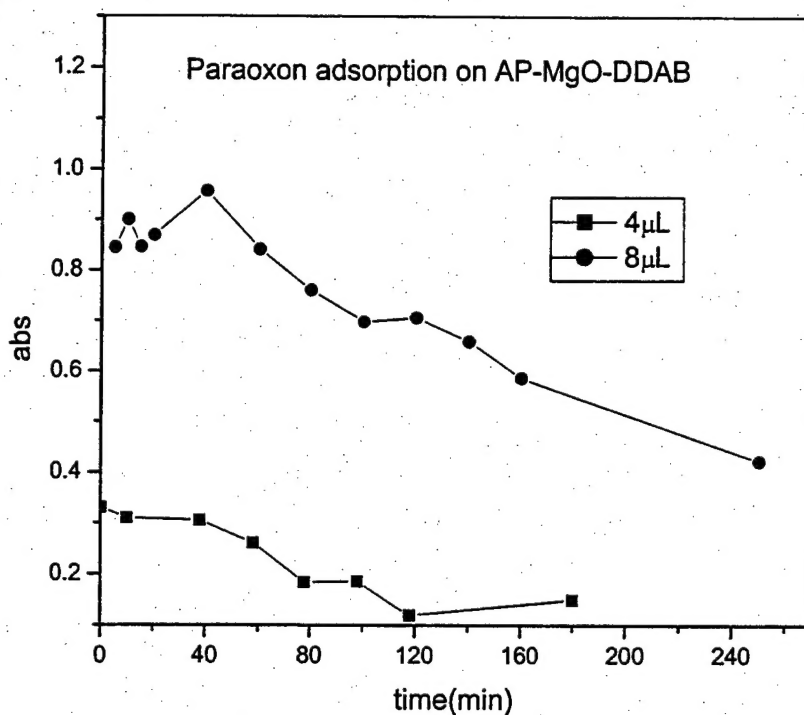**Figure 3:** Destructive adsorption of paraoxon on AOT coated AP-MgO nanoparticles.

Figure 4: Destructive adsorption of paraoxon on DDAB coated AP-MgO nanoparticles.

Table 5: Destructive adsorption of paraoxon in pentane on surfactant coated AP-MgO nanoparticles

Sample	Molar ratio
AP-MgO	1 mol paraoxon:34 mol AP-MgO
AP-MgO-AOT	1 mol paraoxon: 45 mol AP-MgO-AOT
AP-MgO-DDAB	1 mol paraoxon: 77 mol AP-MgO-DDAB

A similar trend in reactivity was observed for the destructive adsorption of 2-CEES on the surfactant coated AP-MgO nanoparticles (Figure 5). AP-MgO-AOT performs better compared to AP-MgO-DDAB but the reactivity of both the samples is less than that of pure AP-MgO. The coating of surfactants does reduce the reactivity of the samples, but

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the reduction in reactivity/capacity for 2-CEES destructive adsorption, is only moderate for AOT, but more significant for DDAB.
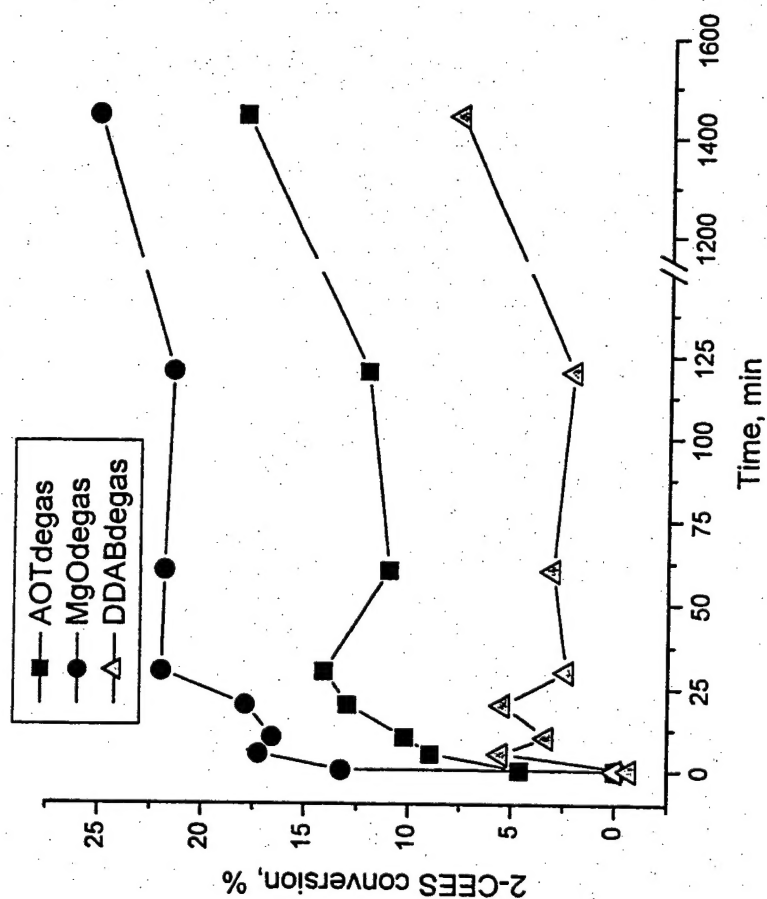

Figure 5: Destructive adsorption of 2-CEES on the surface of surfactant modified AP-MgO nanoparticles.

PUBLICATION: